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Electronic structure and x-ray magnetic dichroism in random substitutional alloys of f -electron elements

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The Koringa-Kohn-Rostoker-coherent-potential-approximation method combines multiple-scattering theory and the coherent-potential approximation to calculate the electronic structure of random substitutional alloys of transition metals. In this paper we describe the generalization of this theory to describe f -electron alloys. The theory is illustrated with a calculation of the electronic structure and magnetic dichroism curves for a random substitutional alloy containing rare-earth or actinide elements from first principles.

The Koringa-Kohn-Rostoker-coherent-potential approximation (KKR-CPA) in both its nonrelativistic and relativistic forms has been a reliable method for calculating the electronic structure of random substitutional alloys from first principles^{1,2} for 15 years. It has proved successful in calculating transition-metal-alloy properties as diverse as electronic structure,³⁻⁵ alloy magnetism,⁶ mechanical properties,⁷ order-disorder transitions,⁸ and in the interpretation of spectroscopies.⁹ For ordered materials the KKR method for calculating electronic structure has been a standard tool for many years, and a relativistic spin-polarized version has been developed.^{10,11} The next step to be taken was to develop the spin-polarized-relativistic version of the theory (SPRKKR-CPA) and this was achieved by Ebert and co-workers^{12,13} and applied to calculate magnetic-dichroism spectra in transition-metal alloys.

It comes as a surprise to discover that, despite its success, the KKR-CPA idea has not been applied to alloys containing rare-earth and actinide elements. This is despite the fact that this region of the Periodic Table contains some of the most fascinating topics in condensed-matter physics such as indirect exchange magnetism, heavy fermions, intermediate valence, localized/itinerant transitions of the f electrons, and a vast array of exotic magnetic structures. In this paper we remedy this situation by describing the generalization of the SPRKKR-CPA to the study of random substitutional alloys containing rare-earth and actinide elements. Furthermore, we are then able to present a density of states calculated from first principles for this class of materials, and we go on to present a calculation of a magnetic-dichroism spectrum for such an alloy.

The CPA theory enables us to calculate configurationally averaged observables in random alloys. Essentially the CPA sets up a lattice of identical effective po-

tentials and the motion of an electron through this lattice is the same, on the average, as the motion of an electron in the random alloy. The potential around each lattice site is described by a single-site scattering t matrix and the multiple scattering is characterized by a scattering-path operator. Consider a binary alloy containing elements A and B at concentrations c and $(1-c)$, respectively, and with a single atom per primitive cell. The CPA condition is that the average scattering from the central site should be the same as in the pure coherent-potential lattice. Written mathematically this gives us an expression for the scattering-path operator of the effective CPA medium in terms of the scattering-path operators associated with the individual elements

$$\tau_{\Lambda\Lambda'}^{\text{CPA}} = c\tau_{\Lambda\Lambda'}^A + (1-c)\tau_{\Lambda\Lambda'}^B. \quad (1)$$

Here Λ and Λ' are quantum numbers defining the representation, $\tau_{\Lambda\Lambda'}^{\text{CPA}}$ can be calculated in terms of the usual KKR structure constants $G(\mathbf{k}, E)$, and an effective single-site scattering t matrix,

$$\tau_{\Lambda\Lambda'}^{\text{CPA}} = \frac{1}{V_{\text{BZ}}} \int_{V_{\text{BZ}}} [(t^{\text{CPA}})^{-1} - G(\mathbf{k}, E)]_{\Lambda\Lambda'}^{-1} d\mathbf{k}, \quad (2)$$

where BZ means Brillouin zone. The standard expression for the effective t matrices is

$$\begin{aligned} (t^{\text{CPA}})^{-1}_{\Lambda\Lambda'} &= c(t^A)^{-1}_{\Lambda\Lambda'} + (1-c)(t^B)^{-1}_{\Lambda\Lambda'} \\ &+ \sum_{\Lambda''\Lambda'''} [(t^A)^{-1}_{\Lambda\Lambda''} - (t^{\text{CPA}})^{-1}_{\Lambda\Lambda''}] \tau_{\Lambda''\Lambda'''}^{\text{CPA}} \\ &\times [(t^B)^{-1}_{\Lambda'''\Lambda'} - (t^{\text{CPA}})^{-1}_{\Lambda'''\Lambda'}]. \end{aligned} \quad (3)$$

The equations above form a self-consistent set that can be solved iteratively.

The important thing to note about Eqs. (1)–(3) is that they do not depend upon the details of the coupling of

the t matrices or the representation. This means that they can be invoked, without change, for the relativistic spin-polarized case where the t matrices with the same value of the l quantum number but different values of j are coupled. The single-site t matrices in this case contain terms which are off diagonal in the quantum numbers and have to be calculated from the Dirac equation for a spin-dependent potential. An efficient method for doing this has been given by Strange and co-workers.^{10,11}

It has been shown by Staunton, Gyorffy, and Weinberger⁴ that the relativistic KKR-CPA applied to a transition-metal alloy involves solving eleven simultaneous CPA equations self-consistently. When we go to the RKKR-CPA for an f -electron alloy this number increases to forty. With the lifting of degeneracies brought about by the magnetism, the full SPRKKR-CPA yields an effective scattering-path operator with 136 nonzero elements of which 84 are independent. So, it is necessary to solve 84 simultaneous CPA equations self-consistently.

It turns out that a direct implementation of Eqs. (1)–(3) is not a computationally efficient method of solving the SPRKKR-CPA equations. Convergence is often difficult to obtain, particularly in regions of the electronic structure where the density of states is large and rapidly varying. Whether convergence is obtained or not often depends upon the arbitrary initial guess made for the effective t matrices. Ebert, Weinberger, and Voitlander¹⁴ and Strange *et al.*¹¹ have solved similar problems of convergence by calculating the electronic structure at complex energies and extrapolating back to the real axis using the Cauchy-Riemann relations. However, this is not always satisfactory or desirable. Therefore we have invoked the procedure suggested by Ginatempo and Staunton,⁵ which itself is based upon earlier work by Mills, Gray, and Kaplan¹⁵ and Butler.¹⁶ It is trivial to manipulate the CPA condition into the following form:⁵

$$c \{ [(t^{\text{CPA}})^{-1} - (t^A)^{-1}]^{-1} - \tau^{\text{CPA}} \}_{\Lambda\Lambda'}^{-1} \\ + (1-c) \{ [(t^{\text{CPA}})^{-1} - (t^B)^{-1}]^{-1} - \tau^{\text{CPA}} \}_{\Lambda\Lambda'}^{-1} = X_{\Lambda\Lambda'}^c, \quad (4)$$

and for a fully converged solution of the CPA $X_{\Lambda\Lambda'}^c = 0$. Ginatempo and Staunton show that $X_{\Lambda\Lambda'}^c$ can be identified with the difference between the current effective medium described by t_i^{CPA} and the next iteration of this quantity t_{i+1}^{CPA} . $X_{\Lambda\Lambda'}^c$ can be used as a tolerance parameter for the CPA. We find that insisting that $X_{\Lambda\Lambda'}^c < 10^{-8}$ for every nonzero element of τ^{CPA} gives a solution to the CPA equations that is sufficiently precise for all applications. With this level of tolerance the SPRKKR-CPA converges remarkably quickly. In regions where the density of states is low and smoothly varying, we find only three or four iterations are required for convergence. Where the density of states is rapidly changing, e.g., in the f -band region in the example below, convergence can take up to 15 iterations. This is the same as has been found for alloys of transition-metal elements.¹⁷

We have consistently used the (κ, m_j) representation, where κ is the usual spin-angular quantum number¹⁸ and m_j is the eigenvalue of the z component of the angular-momentum operator. Hence, in the present paper Λ is a

combined index representing both these quantum numbers. This is not necessary, however; any other representation would be equally valid, and that is why we have used a general index to describe them.

At least up to and including $l=3$, a relativistic spin-polarized CPA does not contain any new off-diagonal elements of τ beyond those already found in a relativistic treatment of ordered magnetic materials. This is due to the fact that the off-diagonal elements introduced by the CPA are just a subset of those introduced by the symmetry breaking due to the relativistic spin-polarized treatment of the scattering theory. Note also that there is coupling that is off diagonal in the l quantum number only between states of even l and states of odd l . The lack of coupling of states of even l to states of odd l reflects the fact that such states have opposite parity.

As in the ordered case, if the magnetic moment points along one of the edges of the crystal unit cell the irreducible section of the Brillouin zone is $\frac{3}{48}$ of the total zone rather than the usual $\frac{1}{48}$. This is due to the symmetry breaking caused by the selection of a direction relative to the crystal lattice by the magnetic moment. Therefore the Brillouin-zone integral of Eq. (2) takes three times longer in this case than the nonmagnetic RKKR-CPA. The Brillouin-zone integral was performed using a ray method as described by Stocks and Winter.¹ With the factors discussed above, and the increase in matrix size from 18×18 to 32×32 , an electronic-structure calculation for a magnetic alloy of rare-earth/actinide elements takes about 100 times more CPU time than a standard relativistic KKR-CPA calculation for a nonmagnetic transition-metal alloy.

The above scheme for solving the relativistic spin-polarized KKR-CPA equations is tractable, but ultimately it can only be judged by its ability to reproduce experimentally verifiable quantities, particularly those that cannot be obtained from a less sophisticated theory. To this end we use the above scheme to calculate the electronic structure of the random substitutional alloy $\text{Ce}_{0.5}\text{Th}_{0.5}$. In Figs. 1(a) and 1(b) we show the f -electron contribution to the density of states of ordered nonmagnetic CeTh on a cesium chloride lattice. These were calculated using the semirelativistic linear-muffin-tin-orbital (LMTO) method. Clearly they are very highly structured and the f bands on the Ce site fall about 0.1 Ry lower than those on the Th site. There is relatively little hybridization between f states on the two sites. In Figs. 2(a) and 2(b) we show the results for the f -electron contribution to the density of states for disordered $\text{Ce}_{0.5}\text{Th}_{0.5}$. These were calculated using the potential from the self-consistent semirelativistic spin-polarized LMTO calculation on ordered CeTh. Comparison with Figs. 1(a) and 1(b) shows the effect of alloying. As one would expect, the density of states has been broadened and smoothed out so that much of the structure has disappeared. The density of states on both the Ce and Th sites can be seen to be split by spin-orbit coupling into $j = \frac{5}{2}$ and $\frac{7}{2}$ bands. In the ordered compound the magnetic moment on the Ce site was $0.11\mu_B$ and on the Th site was $0.02\mu_B$; in the disordered alloy this had been significantly reduced to $0.007\mu_B$ on the Ce site and $0.001\mu_B$ on the Th site (i.e., the magnetic

moment has been almost completely destroyed by the randomization of the lattice-site occupancy). Some further exploratory calculations show that these moments are very sensitive to the lattice constant used. Our lattice constant was taken from Skriver.²⁰ Furthermore, there is now very strong hybridization between the Ce $j = \frac{7}{2}$ states and the Th $j = \frac{5}{2}$ states. Hence these figures suggest that alloying can completely change the nature of the bonding.

Many f -electron materials require a localized description of their magnetic properties.²¹ However, as has been

shown,²² there are also many for which a description based on density-functional theory gives excellent agreement with experiment. $\text{Ce}_{0.5}\text{Th}_{0.5}$ is certainly one of these. A general expression for the x-ray absorption rate of such materials has been derived by Durham.⁹ A relativistic spin-polarized version of this has been written down by Ebert, Strange, and Gyorffy.¹⁹ The only modification to their theory due to the CPA is that the τ that enters the transition-rate expression is replaced by τ^A or τ^B given by Eq. (6), whichever is appropriate, as the x ray is a site-specific probe. In Fig. 3 we have plotted

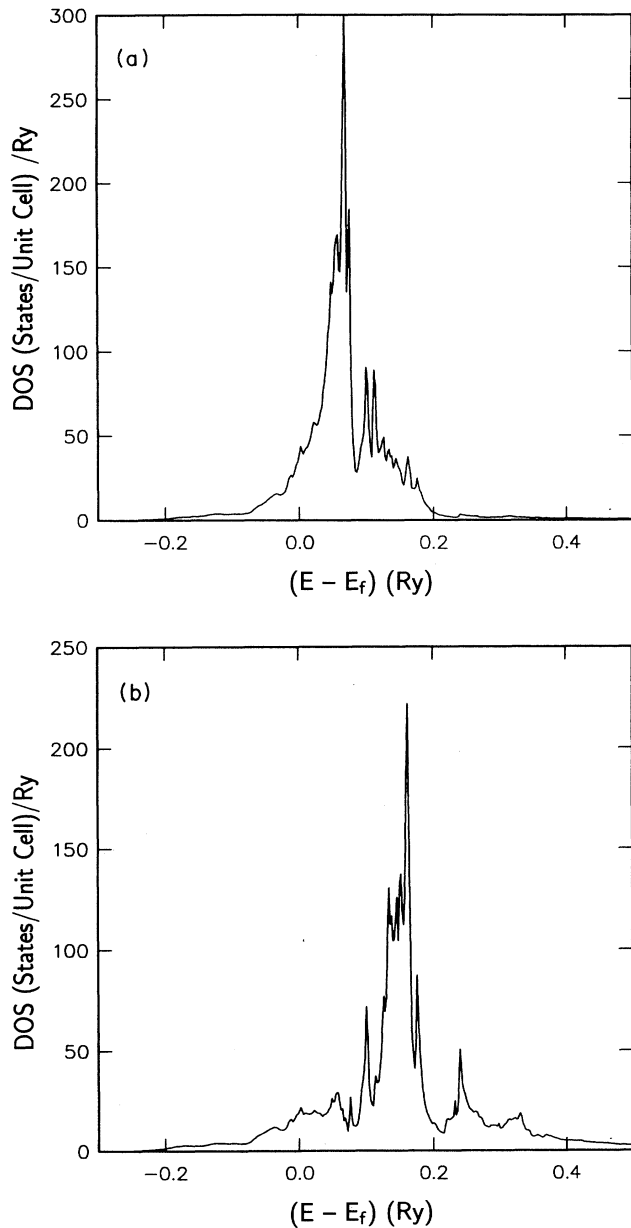


FIG. 1. (a) The f contribution to the density of states on the Ce site in ordered CeTh on a CsCl lattice. (b) The f contribution to the density of states on the Th site in ordered CeTh on a CsCl lattice.

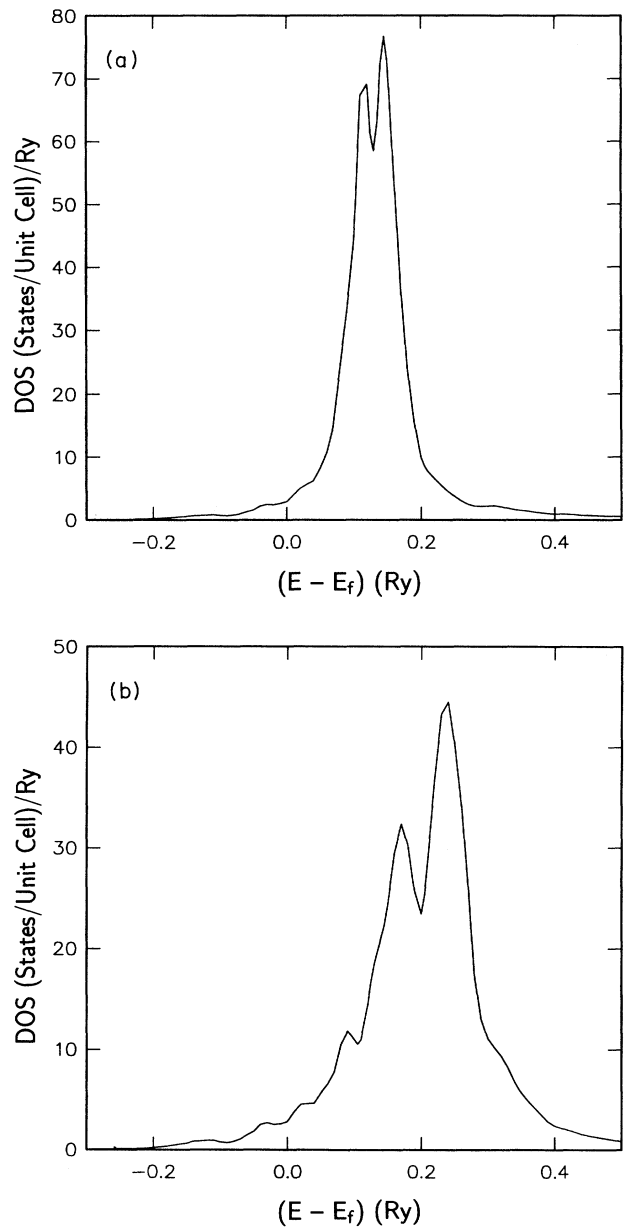


FIG. 2. (a) The f contribution to the density of states on the Ce site in disordered $\text{Ce}_{0.5}\text{Th}_{0.5}$ on a bcc (body-centered-cubic) lattice. (b) The f contribution to the density of states on the Th site in disordered $\text{Ce}_{0.5}\text{Th}_{0.5}$ on a bcc lattice.

the absorption dichroism curves for excitations from the M_{IV} and M_V edges of thorium in disordered $Ce_{0.5}Th_{0.5}$. One would expect dichroism from these edges to be large in a rare-earth or actinide material in general; however, because of the low magnetic moment in this particular material the dichroism signal is only of the order of a few percent. There is a strong correspondence between the peaks in the dichroism curves and the densities of states. The first minimum in the M_{IV} curve corresponds to the $j=\frac{5}{2}$ peak in the Ce density of states. The next maximum corresponds to the Ce $j=\frac{7}{2}$ peak. The next minimum and maximum coincide with the $j=\frac{5}{2}$ and $\frac{7}{2}$ states on the Th site. The very first peak corresponds with the minor peak on the low-energy side of the Th f density of states. There is some correlation between the M_{IV} and M_V edges, although this is not very strong due to the low magnetic moment of this material. In a real experiment much of the structure in Fig. 3 would be washed out by lifetime and instrumental resolution effects. Nonetheless in f -electron alloys where the moment is large and an itinerant view of magnetism is appropriate, structure should survive in the dichroism curves and the present theory should give a good description of it.

In summary, then, we have generalized the SPRKKR-CPA to treat alloys containing rare-earth and/or actinide elements, and have shown that this can yield fundamental information about the nature of the electron states in such alloys. We have used the results to show that there is understanding to be gained on the nature of bonding, and the effect of random-site occupancy on the magnetism. Also we have made a calculation of a magnetic-dichroism curve for such an alloy.

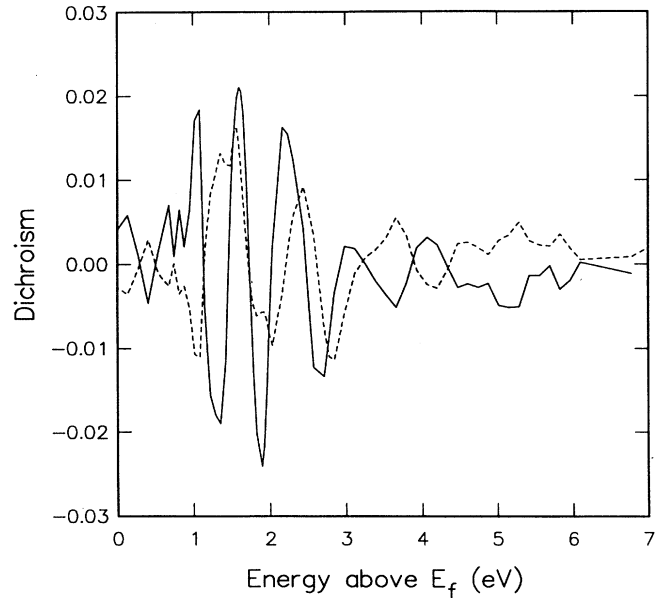


FIG. 3. Magnetic dichroism at the thorium M_{IV} (full line) and M_V (dashed line) edges in disordered $Ce_{0.5}Th_{0.5}$.

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